Chem 41c Final Exam

Stoltz, Spring 2007, June 4, 2007

The exam begins when you turn to page 2. You have 4 hours to complete the exam. This is a closed note and closed book exam with no collaboration. You may use the periodic table on the last page of this packet. You may not use any other materials. The exam has a total of 200 points and counts for 40% of your course grade. Good luck.

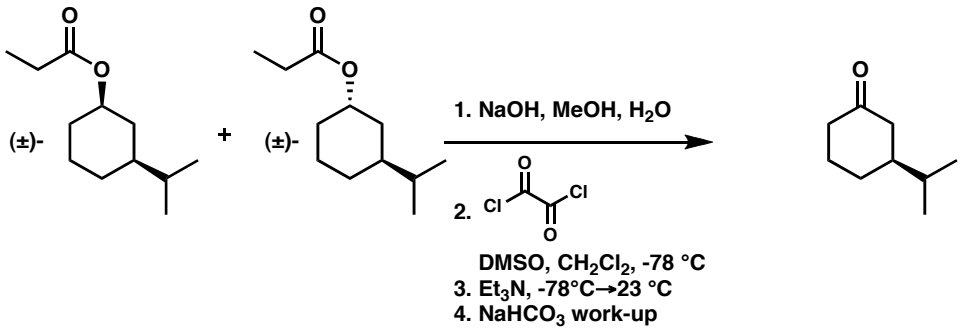
There are 16 pages in this exam packet.

The Exam is due by Friday June 8, 2006 by 5 PM.

*Name:*_____

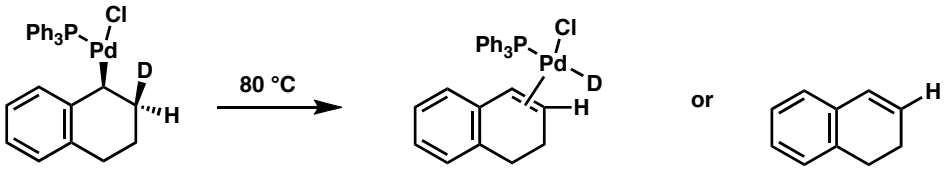
1. Predict the major non-volatile products (if any) of the following reactions or sequences. Clearly mark your answers by placing a **box** around the compound that you believe to be the major product. (5 points each).

a.

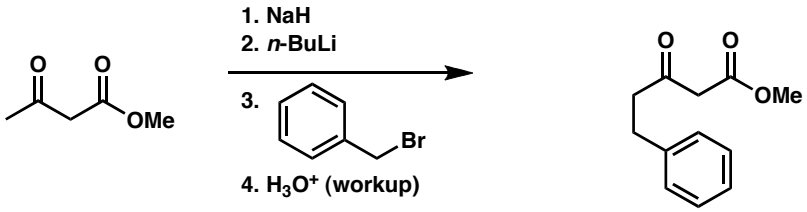


hint: one racemic non volitile product is formed

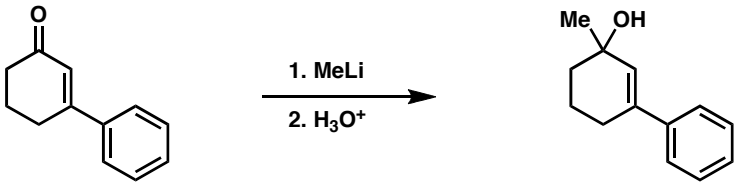
b.



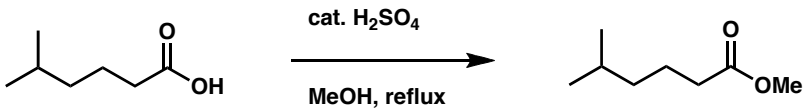
c.



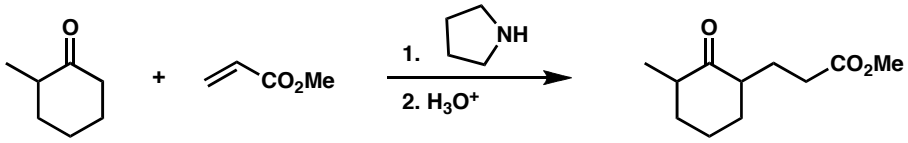
d.


O
1. MeLi
2. H3O+
Me
OH

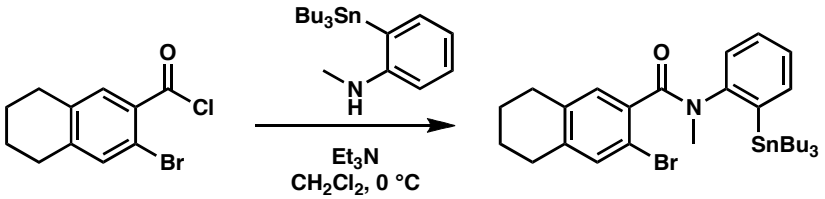
e.


O
OH
cat. H2SO4
MeOH, reflux
O
OMe

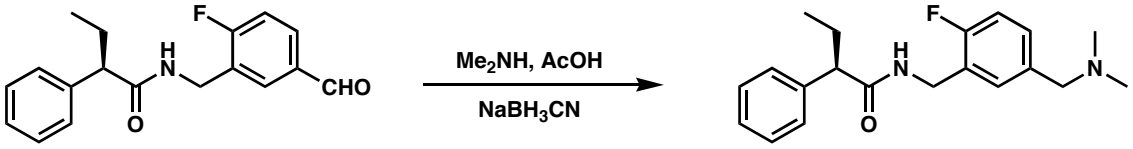
f.


O
+
CO2Me
1.
NH
2. H3O+
O
CO2Me

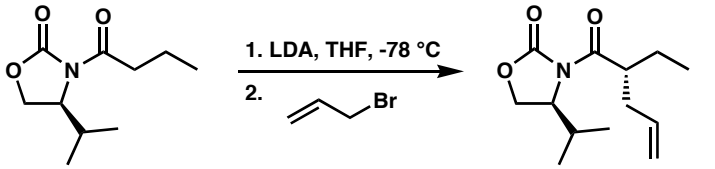
g.



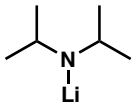
h.



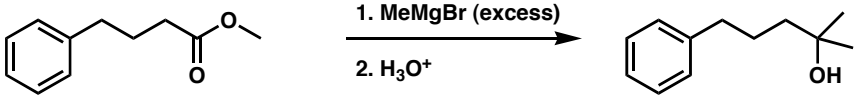
i.



5 point bonus: what is the structure of LDA?

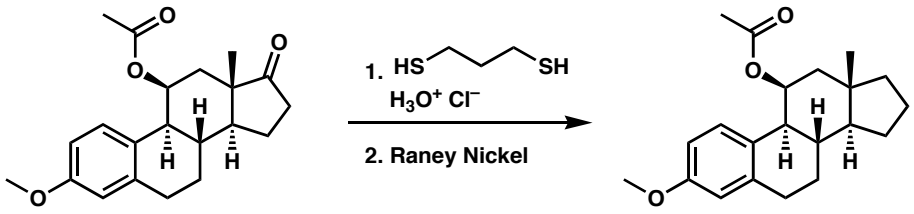


j.



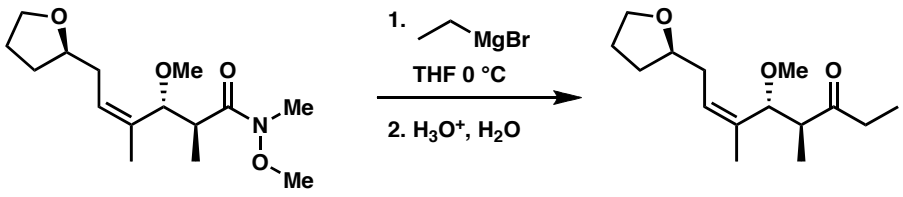
2. Provide reagents for the following transformations. They may be multistep processes, but should not be longer than 5 steps. (5 points each)

a.

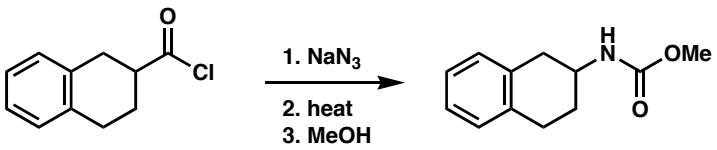


(maybe Clemmenson...not Wolf Kischner)

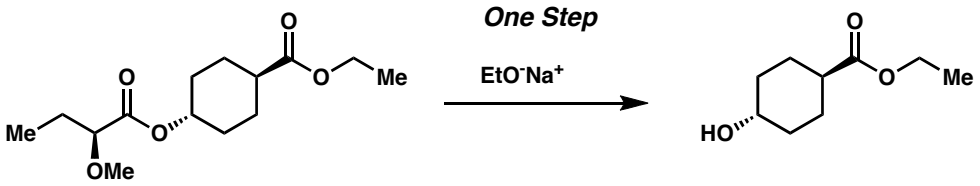
b.



c.

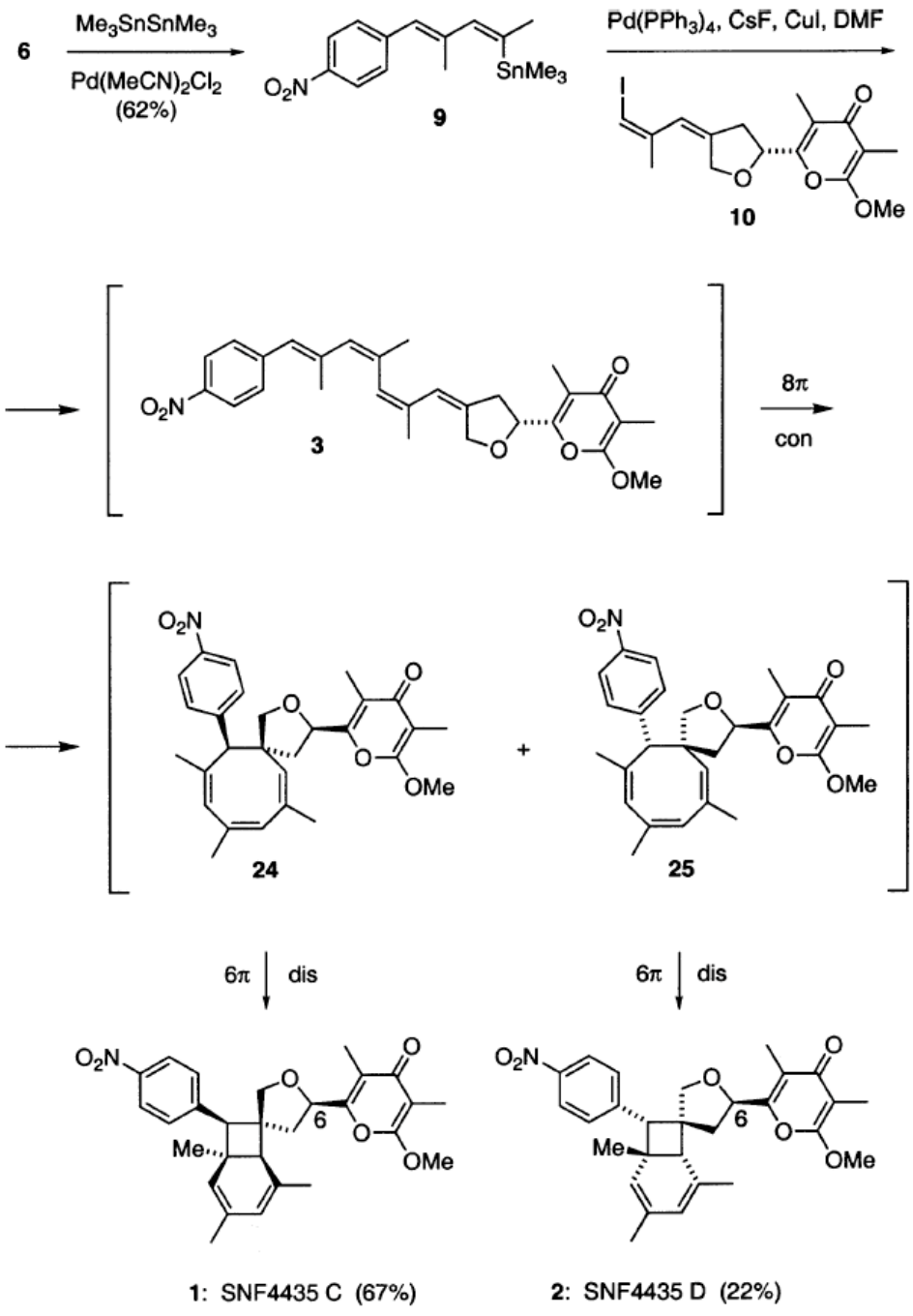


d.

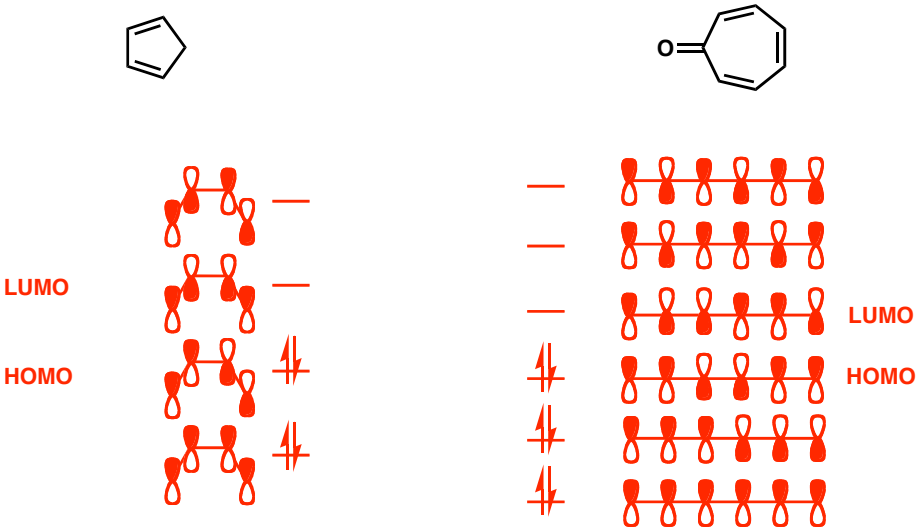


3. We have learned about transition metal-catalyzed processes and pericyclic reactions this term. A remarkable cascade of such reactions was recently reported to produce the unusual and interesting natural products SNF4435 C and D (compounds **1** and **2**). Scheme 5 is taken directly from the paper that describes their synthesis. Given your knowledge of these reactions, 1) predict the structure of intermediates **3**, **24**, and **25** 2) Describe a mechanism for the the conversion of **3** to **24** and **25**, and from **24** and **25** to **1** and **2** (hint: it may be useful to draw an orbital diagram for **3** although not neccessary) and 3) As a bonus provide a possible structure for **6**. (20 points, 10 point bonus)

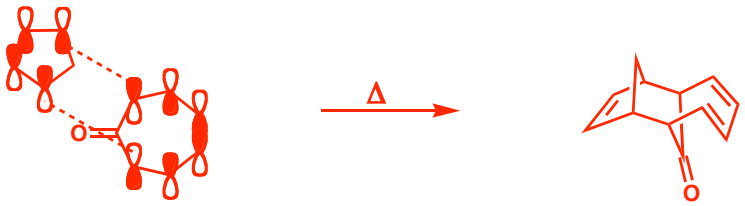
Scheme 5



4. a) Draw the molecular orbitals for the olefin-containing portions of the following conjugated systems. Fill in the electrons and label the HOMO and LUMO for each system.. (5 points)

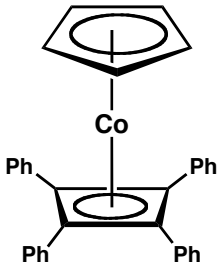


b) Predict the product of the thermal [6+4] cycloaddition of these two compounds. Is the process allowed by frontier molecular orbital theory? Hint: Draw the compounds with the appropriate molecular orbitals first. (5 points)



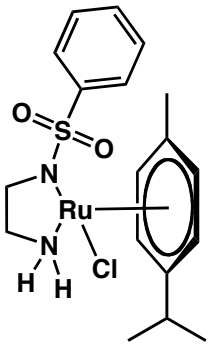
5. In the following complexes, what is the formal oxidation state of the metal, the d^n description, and the electron count? Feel free to use the periodic table in the room (5 points each-no partial credit)

a.



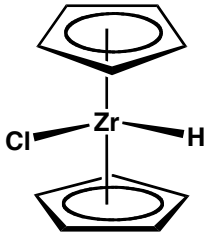
Co(I) or Co^{1+} **d^8** **18 electron complex**

b.



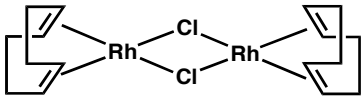
Ru(II) or Ru^{2+} **d^6** **18 electron complex**

c.



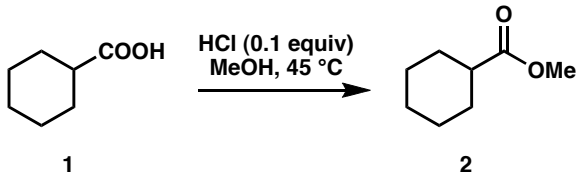
Zr(IV) or Zr^{4+} **d^0** **16 electron complex**

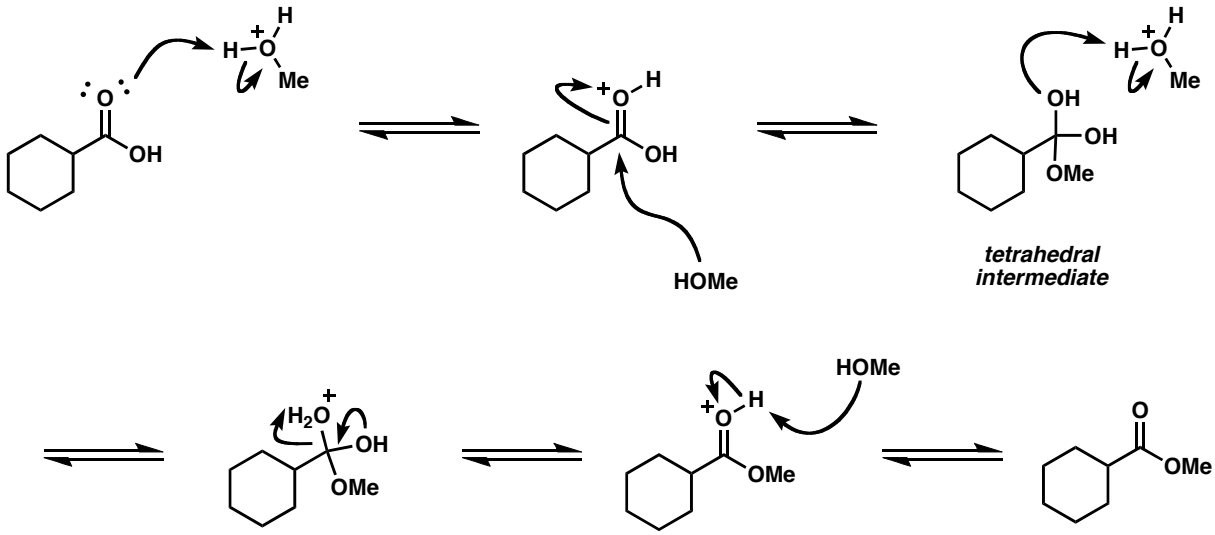
d.



Rh(I) or Rh^{+1} **d^8** **16 electron each Rh**

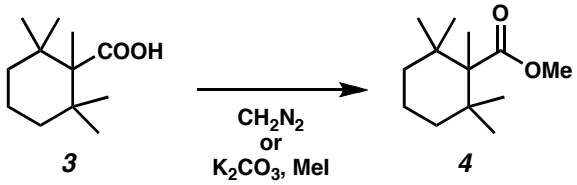
6. a) Provide a detailed curved arrow mechanism for the following reaction. What drives the equilibrium to the product side? (10 points)



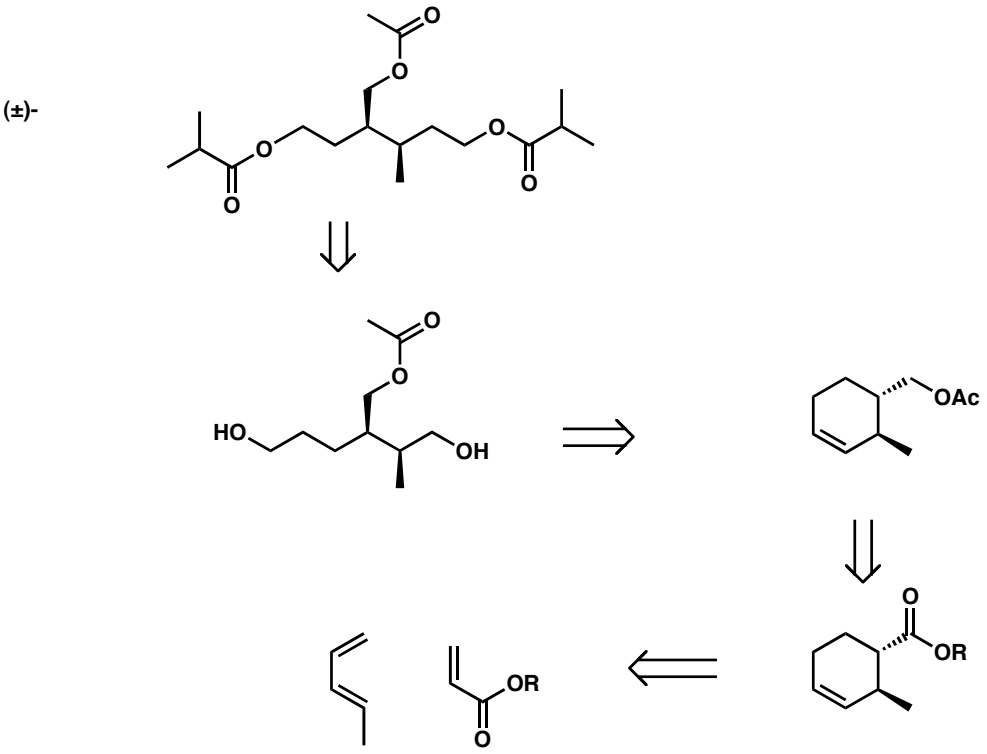


Reaction driven to completion due to large excess of alcohol (MeOH).

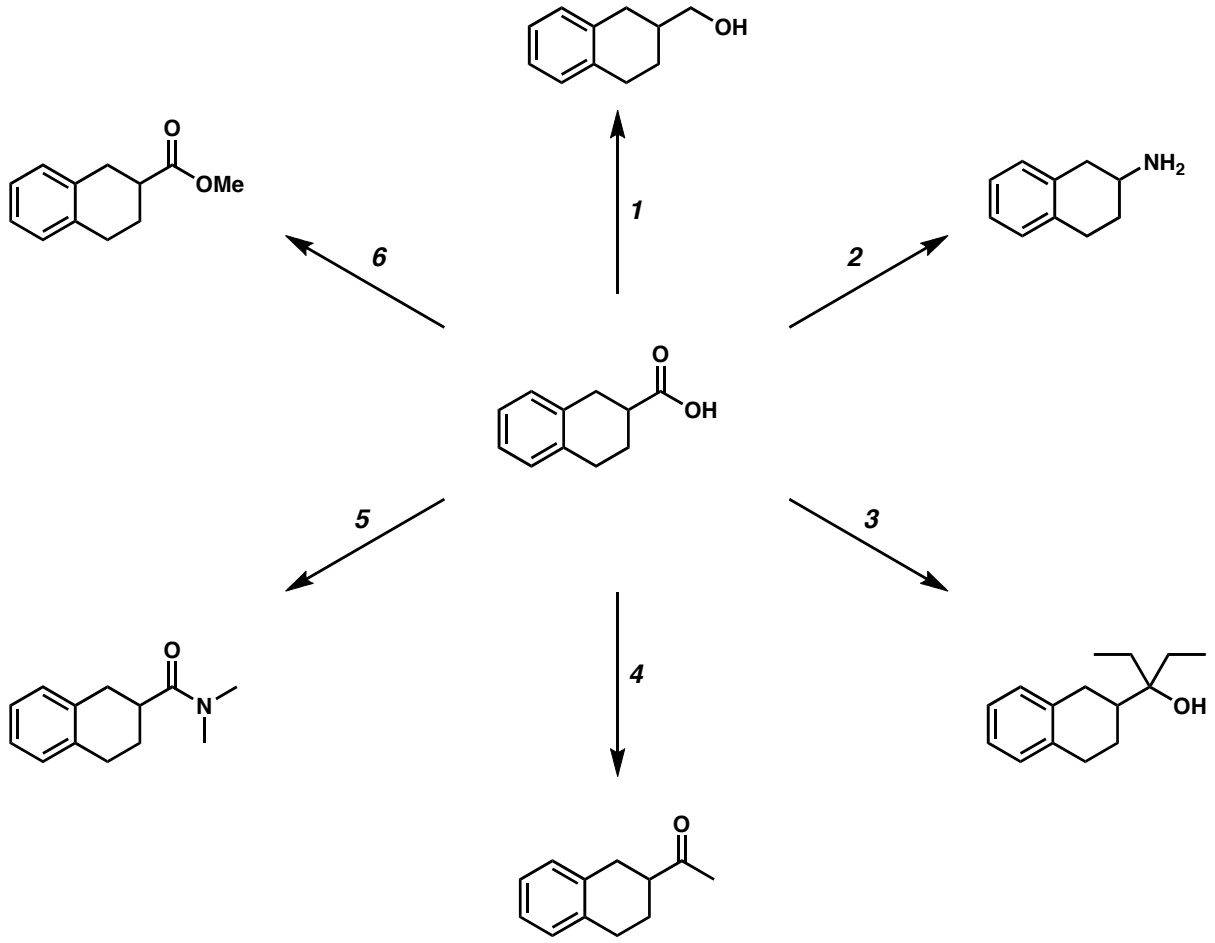
b) In contrast to part a of this problem, under the same conditions the following reaction (**3**→**4**)is extremely slow. Why do you think this is the case? Provide an alternative method for preparing the methyl ester **4** from carboxylic acid **3** that you believe would be fast and high yielding. Provide a detailed curved arrow mechanism for your new synthesis of **4** from **3** and explain why the new method should be better. (10 points)



7. Imagine yourself in graduate school (let's say in 2011)...On a late summer afternoon, a good Bostonian friend of yours from the lab presents you with the opportunity to see the first place Red Sox play the bottom feeder New York Yankees at Fenway Park the following afternoon. Since you are in California, you will need to catch the red-eye that night in order to make the first pitch the next day. You are in desparate need of bulletproof route to your target molecule (**1**), so that your SURF student will have something to do besides playing video games and washing dishes. Design a retrosynthesis of **1** and a outline a complete forward synthesis for the following compound as a single diastereomer (in racemic form) starting from fragments of less than 6 carbons (or benzene). Just think, if you complete your task on time, you will not only get to witness four-time Cy Young award winner Daisuke Matsuzaka pitch for the perrenial World Champion Boston Red Sox, but your SURF student will complete your project by the time you get back to Cali! (20 points)



8. As you can see, carboxylic acids are valuable synthons in organic chemistry. Provide reagents for each of the following six transformations in the spaces below the figure. Keep in mind that some transformations may require more than one step. (20 points)



1. _____**$LiAlH_4$**_____

   _____

   _____

2. _____**1._$SOCl_2$**_____

   _____**2._NaN_3, then Δ**_____

   _____**3._H_2O**_____

3. _____**1._CH_2N_2**_____

   _____**2. EtMgBr (excess)**_____

   _____

4. _____**1._$SOCl_2$**_____

   _____**2._HN(OMe)Me_____

   _____**3._MeMgBr_____

5. _____**1._$SOCl_2$**_____

   _____**2._Me_2NH**_____

   _____

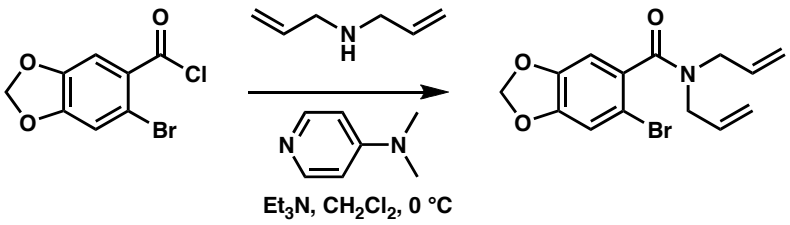
6. _____**MeOH, H+__or__CH_2N_2**_____

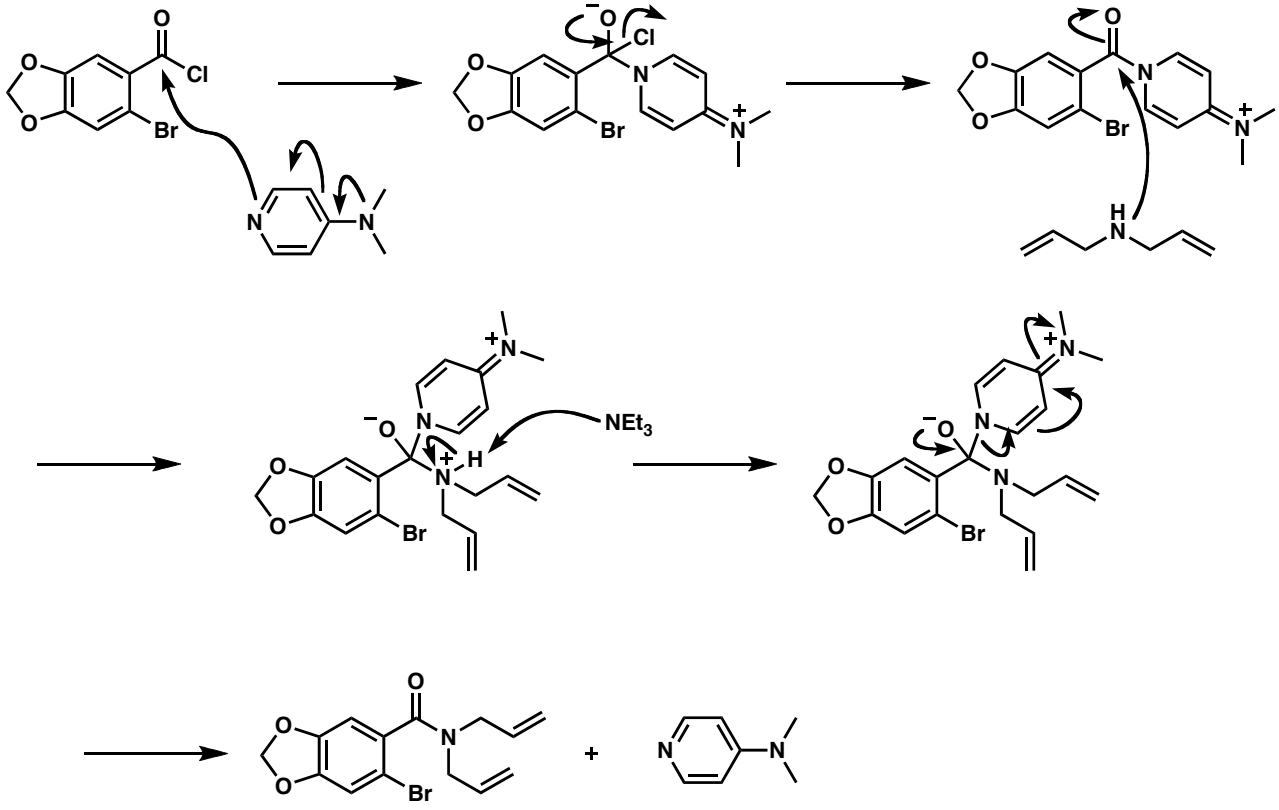
   _____

   _____

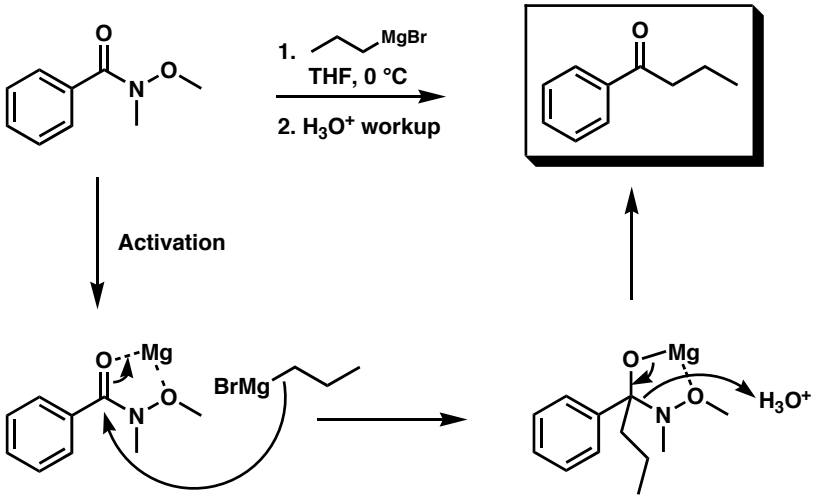
9. Predict the product of these reactions and provide curved arrow mechanisms for each. (20 points)

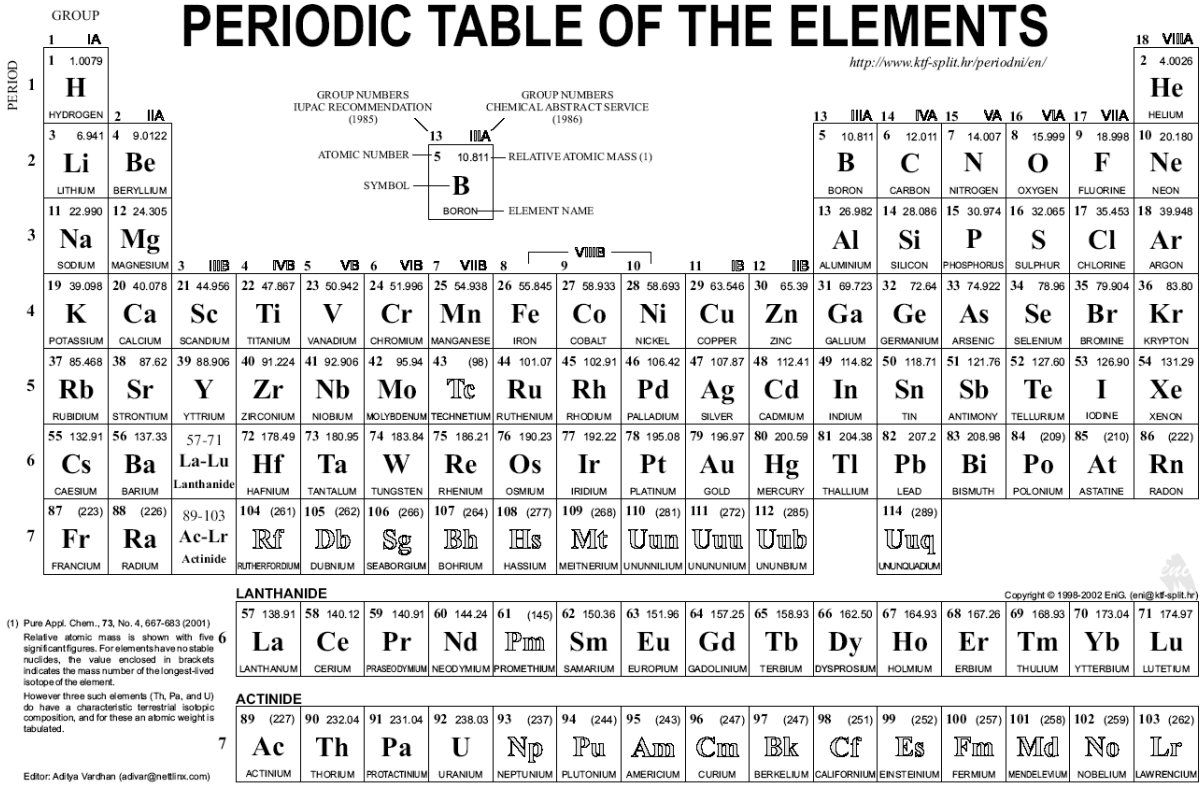
a.





b.




PERIODIC TABLE OF THE ELEMENTS
http://www.ktf-split.hr/periodni/en/
GROUP
PERIOD
GROUP NUMBERS IUPAC RECOMMENDATION (1985)
GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)
ATOMIC NUMBER
SYMBOL
RELATIVE ATOMIC MASS (1)
ELEMENT NAME
LANTHANIDE
ACTINIDE
(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.
Editor: Aditya Vardhan (adivar@netlinx.com)
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The End